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STUDIES ON THE SYNTHESES OF
BORON HYDRIDE SYSTEMS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The boron hydrides B_2H_6, B_4H_{10}, B_5H_{11}, and $B_{10}H_{14}$ are prepared in good yields through hydride ion abstraction reactions when the borane anions BH_4^-, $B_3H_8^-$, $B_4H_9^-$, and $B_9H_{14}^-$, respectively, are treated with a molar equivalent of a Lewis acid BX_3 (X=F,Cl, or Br), generally in the ansence of a solvent, for reaction periods of 1-4 hrs. A high yield (up to 90%) method for the conversion of B_5H_9 to $B_9H_{14}^-$ is presented as the precursor to the practical

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conversion of B_5H_9 to $B_{10}H_{14}$ (up to (50%). Additionally a good conversion of B_5H_9 to $\eta-B_{18}H_{22}$ (up to (50%) and the preparation of the <u>nido</u>-carborane $\phi_2C_2B_8H_{10}$ have been achieved. The hydride ion abstraction reactions by BBr_3 and BCl_3 lead to the new anions $HBBr_3^-$ and $HBCl_3^-$.

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Forward

In the past three years under ARO support, we have developed a new approach to boron hydride syntheses[1] which has led to convenient high yield preparations of B_4H_{10} and B_5H_{11} by procedures which are safer, cleaner, and more easily scaled-up than the standard pyrolytic and chemical methods. Additionally, this new approach has led to a practical and simple conversion of B_5H_9 to $B_{10}H_{14}$ in a "one-pot" reaction. This latter result is of special significance in that 200,000 pounds of B_5H_9 is in storage, a legacy from the high energy fuels program from the 1950's. Thus there is the potential for putting this B_5H_9 to good use in preparing $B_{10}H_{14}$ which is currently in short supply. The U.S. Army has applied for a patent for this procedure. Furthermore, in the course of our work under ARO support we have developed additional chemistry of B_5H_9 which leads to a high yield preparation of $B_9H_{14}^-$ (90% yield), a good conversion of B_5H_9 to $B_{18}H_{22}$ (ca 50%), and most recently the preparation of the nido-carborane $\phi_2C_2B_8H_{10}$. In effect, B_5H_9 can be considered to be a raw material which can be the starting point for preparing materials which are normally prepared from $B_{10}H_{14}$ from B_5H_9 or proceeding directly to materials which are normally synthesized from $B_{10}H_{14}$. Principles which have been developed for the preparation of $B_{10}H_{14}$, B_5H_{11}, and B_4H_{10} have also been applied to the development of a high yield synthesis (up to 90%) of B_2H_6 in a procedure which does not require a solvent. The Ohio State University has applied for a patent on this process.
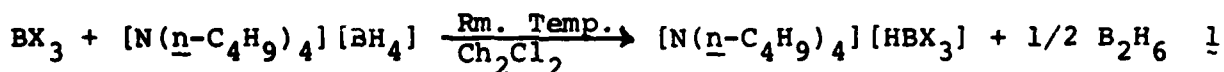
The above statements briefly summarize background information to the proposed program. Details are provided below.

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Results and Discussion

1. Hydride Ion Abstraction Reactions: New, Systematic Good Yield Syntheses of B_4H_{10}, B_5H_{11}, and $B_{10}H_4$
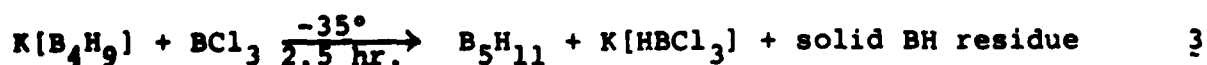
We have developed a new systematic approach to boron hydride syntheses which is based upon the principle of hydride ion abstraction.

The systematic nature of these syntheses relates to our observation that hydride ion can be abstracted from certain boron hydride anions to give as one of the final products a neutral boron hydride which contains one more boron atom than the anionic starting material. The simplest reaction observed involves $[N(n\text{-}C_4H_9)_4][BH_4]$ and is quantitative

$$BX_3 + [N(n\text{-}C_4H_9)_4][BH_4] \xrightarrow[\text{Ch}_2\text{Cl}_2]{\text{Rm. Temp.}} [N(n\text{-}C_4H_9)_4][HBX_3] + 1/2\ B_2H_6 \quad \underline{1}$$

where $BX_3 = BCl_3$, BBr_3. The tetra-n-butyl ammonium salts of the previously unreported anions $HBBR_3^-$ and $HBCl_3^-$ are stable, free flowing solids under a dry atmosphere at room temperature. Very recently we have discovered that $NaBH_4$ can react quantitatively with BF_3 in the absence of a solvent to give high purity B_2H_6. This "dry" preparation of B_2H_6 is a potentially practical synthesis.

Tetraborane(10) and pentaborane(11) are prepared by the following reactions in which 1:1 molar ratios of reactants are stirred vigorously in the absence of a solvent.

$$[N(n\text{-}C_4H_9)_4][B_3H_8] + BBr_3 \xrightarrow[\text{1 hr}]{0°} B_4H_{10} + [N(n\text{-}C_4H_9)_4][HBBr_3] + \text{solid BH residue} \quad \underline{2}$$

$$K[B_4H_9] + BCl_3 \xrightarrow[\text{2.5 hr.}]{-35°} B_5H_{11} + K[HBCl_3] + \text{solid BH residue} \quad \underline{3}$$
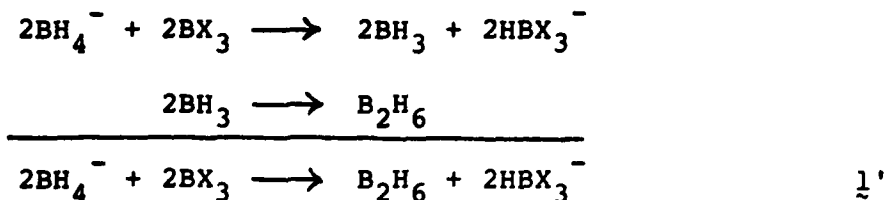
Tetraborane(10) and pentaborane(11) are obtained in 65% and 60% yields, respectively. These yields are based upon the amount of boron in the borane anion. In both reactions the borane anion is completely consumed. The starting material $[N(\underline{n}-C_4H_9)_4][B_3H_8]$ is well known and of course KB_4H_9 is easily obtained from the B_4H_{10} prepared in the reaction cited on page 4. We routinely prepare B_4H_{10} and B_5H_{11} in 10 to 20 millimole quantities in the time frames cited above. Scale-up to larger quantities is practical.

One of the principal handicaps to investigating the chemistry of the intermediate boron hydrides B_4H_{10} and B_5H_{11} has been the absence of simple preparative procedures which would provide these materials in relatively large quantities in good yield. Traditionally, B_4H_{10} and B_5H_{11} have been prepared by hot-cold reactor techniques[2,3] and more recently from the protonation of $B_3H_6^-$ salts.[4-6] Additionally B_5H_{11} has been prepared from the protonation[5b] of $B_5H_{12}^-$. The procedures outlined here are much safer and simpler than the classical hot cold reactor techniques. Additionally, requirements for product purification are minimal for the present method compared to the hot-cold reactor methods and the method of protonation of $B_3H_8^-$ salts. When carried out under conditions indicated, the presence of volatile impurities (trace quantities of B_2H_6 and B_5H_9 from reaction 2 and trace quantities of $\underline{n}-B_9H_{15}$ from reaction 3 present no problems in purifying B_4H_{10} and B_5H_{11}. Our present method for preparing B_5H_{11} is also superior to the earlier reported protonation of $B_5H_{12}^-$ since it gives comparable yields but requires one less step in the preparative procedure.
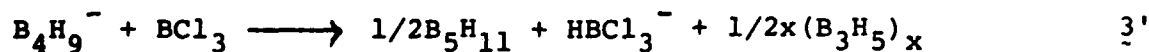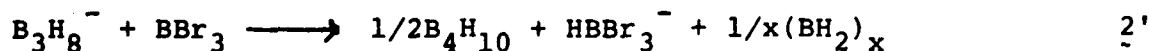
Reaction 1 can be viewed as hydride abstraction from BH_4^- ions to

give BH_3 units which combine to form B_2H_6.

$$2BH_4^- + 2BX_3 \longrightarrow 2BH_3 + 2HBX_3^-$$

$$2BH_3 \longrightarrow B_2H_6$$

$$\overline{2BH_4^- + 2BX_3 \longrightarrow B_2H_6 + 2HBX_3^-} \qquad\qquad \underset{\sim}{1}'$$

This reaction differs from the traditional syntheses of B_2H_6 in which diborane(6) is generated through hydride-halide exchange in reactions of metal borohydrides with solvents.[7-9]

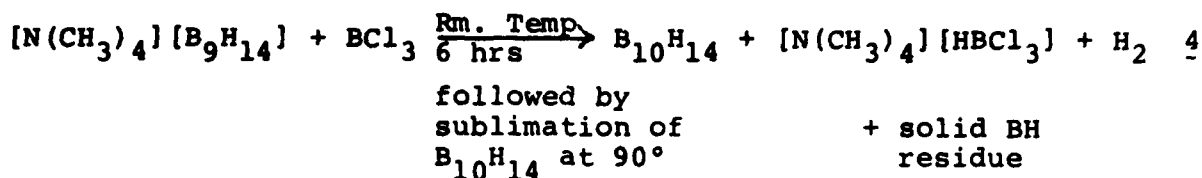For reactions $\underset{\sim}{2}$ and $\underset{\sim}{3}$ hydride abstraction would yield the boranes B_3H_7 and B_4H_8 respectively. In view of the products obtained, it is reasonable to assume that subsequent reactions involve, effectively, transfer of BH_3, for example from one B_4H_8 to another B_4H_8 to produce B_5H_{11}. Indeed very recent results we have obtained which are described in the Proposed Investigation Section of this proposal support this reaction scheme. Thus, viewing reactions $\underset{\sim}{2}$ and $\underset{\sim}{3}$ in this light suggests the following stoichiometries.

$$B_3H_8^- + BBr_3 \longrightarrow 1/2B_4H_{10} + HBBr_3^- + 1/x(BH_2)_x \qquad\qquad \underset{\sim}{2}'$$

$$B_4H_9^- + BCl_3 \longrightarrow 1/2B_5H_{11} + HBCl_3^- + 1/2x(B_3H_5)_x \qquad\qquad \underset{\sim}{3}'$$
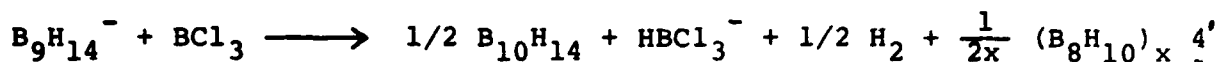
In these reactions 67% of the available boron in $B_3H_8^-$ is converted to B_4H_{10} and 63% of the available boron in $B_4H_9^-$ is converted to B_5H_{11}. The close correspondence of experimental yields to these proposed stoichiometries ($\underset{\sim}{2}'$ and $\underset{\sim}{3}'$) suggests that within experimental error reactions $\underset{\sim}{2}$ and $\underset{\sim}{3}$ are quantitative with respect to yields of B_4H_{10} and B_5H_{11}. Residues of empirical compositions $(BH_2)_x$ and $(B_3H_5)_x$ decompose at room temperature to give small amounts of B_5H_9 and $\underline{n}$-B_9H_{15} respectively.

The systematic nature of this procedure was further demonstrated in an extension of reactions $\underset{\sim}{2}$ and $\underset{\sim}{3}$. Treatment of $[N(CH_3)_4]B_9H_{14}$ with BCl_3 gave $B_{10}H_{14}$ in a yield of 50% based on $B_9H_{14}^-$ (Reaction $\underset{\sim}{4}$).

$$[N(CH_3)_4][B_9H_{14}] + BCl_3 \xrightarrow[\text{6 hrs}]{\text{Rm. Temp}} B_{10}H_{14} + [N(CH_3)_4][HBCl_3] + H_2 \quad \underline{4}$$

followed by
sublimation of   + solid BH
$B_{10}H_{14}$ at 90°   residue

A reaction stoichiometry analogous to $\underline{2}'$ and $\underline{3}'$ is suggested
(Reaction $\underline{4}'$)

$$B_9H_{14}^- + BCl_3 \longrightarrow 1/2\ B_{10}H_{14} + HBCl_3^- + 1/2\ H_2 + \frac{1}{2x}\ (B_8H_{10})_x \quad \underline{4}'$$

In this stoichiometry 56% of the boron in $B_9H_{14}^-$ is converted to $B_{10}H_{14}$,
which corresponds well with our results and is consistent with reaction
$\underline{4}$ being close to quantitative.

2. The Use of Pentaborane(9) as a Starting Material for the Preparation of Higher Boron Hydrides and Carborane Systems

Described here are our recent studies which have led to the practical
conversion of B_5H_9 to $B_9H_{14}^-$, $B_{10}H_{14}$, $B_{18}H_{22}$, $B_9H_{13}L$, and most recently
the nido-carborane system $R_2C_2B_8H_{10}$. The key to this work is our develop-
ment of a good high yield conversion of B_5H_9 to $B_9H_{14}^-$ which is described
below.

a. $\underline{B_9H_{14}^-}$. Although $B_9H_{14}^-$ is generally prepared through the
degradation of $B_{10}H_{14}$ by base,[10] it is also possible to prepare this ion
through the thermal decomposition of $B_5H_8^-$ which is generated by deproton-
ating B_5H_9. However, the yields of $B_9H_{14}^-$ prepared this way from B_5H_9 do
not exceed 60%.[11-14] By allowing $B_5H_8^-$ to react with an equimolar amount
of B_5H_9 in THF at room temperature we have been able to obtain good
quality $B_9H_{14}^-$ in 90% yield.[15] This is achieved experimentally by treating
B_5H_9 with NaH in a 2:1 molar ratio. Although not described here, we have
examined in detail the reaction of $B_5H_8^-$ with B_5H_9 not only to optimize
the yield and purity of $B_9H_{14}^-$, but also to identify intermediates formed
in the overall reaction scheme. We have prepared, according to our par-
ticular needs the salts $[N(\underline{n}-C_4H_9)_4][B_9H_{14}]$, $Na[B_9H_{14}]$ and $K[B_9H_{14}]$.

b. $B_{10}H_{14}$. Our high yield preparation of $[N(\underline{n}\text{-}C_4H_9)_4][B_9H_{14}]$ coupled with our preparation of $B_{10}H_{14}$ from the reaction of $[N(\underline{n}\text{-}C_4H_9)_4][B_9H_{14}]$ with BCl_3 provides a practical route to $B_{10}H_{14}$ from B_5H_9 employing a single reactor for the entire procedure.

In a typical preparation of $B_{10}H_{14}$ from B_5H_9, 21.6 millimoles of NaH, 43.2 millimoles of B_5H_9 and 22 millimoles of $[N(CH_3)_4]Cl$ are stirred for 12 hrs. in 16 ml of THF at room temperature. Hydrogen gas and THF are pumped away, leaving behind a dry solid which is good quality $[N(CH_3)_4]$ $[B_9H_{14}]$ and NaCl. Then 22 millimoles of BCl_3 are condensed onto the solid reaction products and this mixture is stirred vigorously for 6 hrs at 25°. The $B_{10}H_{14}$ is then sublimed from the flask under dynamic vacuum. A 9.57 mmole quantity of $B_{10}H_{14}$ representing a 45% conversion of B_5H_9 to $B_{10}H_{14}$ is obtained. This percent conversion of starting material to $B_{10}H_{14}$ is comparable to that reported for the conversion of $NaBH_4$ to $B_{10}H_{14}$ by a nonpyrolytic method.[16] The present procedure, however, requires fewer steps, less solvent, and it also can be scaled-up.
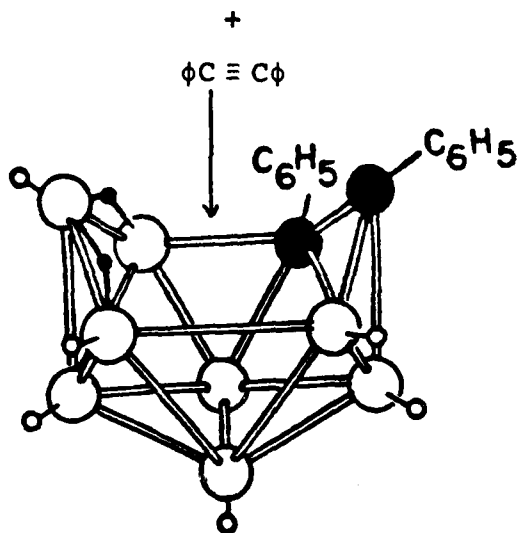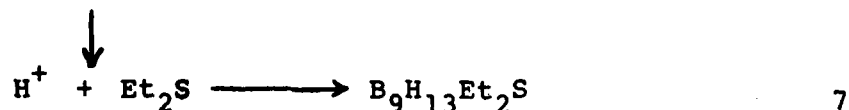
Very recently we have been able to modify the preparation of $B_{10}H_{14}$ to give a more effective conversion of B_5H_9 to $B_{10}H_{14}$. Details of this modification and the principles behind it are discussed in the Proposed Program Section of this proposal since we hope to use this modification in a general way in our systematic synthetic procedures which are based upon hydride ion abstraction reactions.

c. $B_9H_{13}L$ and $\underline{n}\text{-}B_{18}H_{22}$. By taking advantage of the simple high-yield conversion of B_5H_9 to $B_9H_{14}^-$ described above, we found that it is possible to convert B_5H_9 to $B_9H_{13}L$, where $L = Et_2S$, $P\phi_3$ and $\underline{n}\text{-}B_{18}H_{22}$ in practical "one-pot" procedures which are modifications of an earlier method[17]. For example, $B_9H_{14}^-$ is converted to $B_9H_{13}OBu_2$ according to the reaction.

$$B_9H_{14}^- + HCl + Bu_2O \longrightarrow B_9H_{13}OBu_2 + H_2 + Cl^- \qquad \underline{5}$$

Pyrolysis of $B_9H_{13}OBu_2$ gave $\underline{n}\text{-}B_{18}H_{22}$ in a yield which represented a 45% conversion of B_5H_9. This procedure for the preparation of $\underline{n}\text{-}B_{18}H_{22}$ not only frees us of the requirement of $B_{10}H_{14}$, but it also rivals in terms of simplicity and yield other procedures[18] for the preparation of this compound.

d. $5,6\text{-}\phi_2C_2B_8H_{10}$. We have succeeded in preparing from B_5H_9 the the $\underline{nido}$ carborane $5,6\text{-}\phi_2C_2B_8H_{10}$ in a "one-pot" synthesis.

$$2B_5H_9 + NaH \xrightarrow{\text{THF}} Na[B_9H_{14}] \qquad \underline{6}$$

$$H^+ + Et_2S \longrightarrow B_9H_{13}Et_2S \qquad \underline{7}$$

$$+$$

$$\phi C \equiv C\phi$$

$$\underline{8}$$

Normally this $\underline{nido}$ carborane is prepared[19] from a higher carborane system through a degradation process or from the degradation of B_9H_{15} or B_8H_{12}. These earlier methods were dependent upon $B_{10}H_{14}$ since it is the common starting point not only for the higher carboranes but has also been used[10] to prepare $B_9H_{14}^-$ which is then converted to B_9H_{15} and B_8H_{12}.[20]

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Patents Applications

1. "Preparation of Decaborane 14 Through Hydride Ion Abstraction Reactions". Filed by U.S. Army Missle Command. Redstone Arsenal.

2. "A Dry Process for Producing Diborane. Filed by Ohio State University".

Special Technical Reports

Submitted to ARO

1. "Studies on the Conversion of Pentaborane(9) to Decaborane(14)" Part I.

2. "Studies on the Conversion of Pentaborane(9) to Decaborane(14)" Part II.

3. "Studies on the Conversion of Pentaborane(9) to Decaborane(14)" Part III.

Appendix

Publications

1. "New Systematic, Good Yield Syntheses of Boron Hydrides: Preparation of B_4H_{10} and B_5H_{11}. A Practical Conversion of B_5H_9 to $B_{10}H_{14}$", J. Am. Chem. Soc. 1981, 103, 988.

2. "New Systematic Syntheses of Boron Hydrides Via Hydride Ion Abstraction Reactions: Preparation of B_2H_6, B_4H_{10}, B_5H_{11} and $B_{10}H_{14}$". Inorg. Chem. In press.

3. "Hexaborane(10)Derivatives: Relative Acidities of 2-$CH_3B_6H_9$ and 2-BrB_6H_9 and NMR Spectra of 2-$CH_3B_6H_8^-$, 2$BrB_6H_8^-$, and $(THF)_2 Mg(2-CH_3B_6H_8)_2$". Inorg. Chem. 1981, 20, 1270.

4. "Neutron and X-ray Diffraction Studies of Tris(methyl-diphenylphosphine)[tetrahydroborato(1-)copper, $Cu[P(C_6H_5)_2(CH_3]_3(BH_4)$. The First Accurate Characterization of an Unsupported Metal-Hydrogen-Boron Bridge Bond". J. Am. Chem. Soc., 1981, 103, 5165.

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